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14. ABSTRACT

The state-of-the-art hypergol combination currently used in the US for many space propulsion applications consists of monomethyl hydrazine, as the fuel, and nitrogen tetroxide, as the oxidizer. The Air Force Research Laboratory is developing new hypergolic fuels which will provide enhanced performance capabilities as well as improved affordability and efficiency. Furthermore, handling of these new hypergolic fuels is also expected to have a much smaller logistical footprint due to the fact that they are being designed to be environmentally benign. However, practical realization of these hypergols in spacecraft propulsion systems will only come after attaining a satisfactory understanding of how to optimize their combustion characteristics in relevant operating environments. Here we report theoretical results obtained on the prototypical radical-radical reaction: NO_2 + N_2H_3, and the progress made towards building an apparatus consisting of laser photolysis/fast flow-tube reactor coupled to a mass spectrometer for investigating the kinetics of this elementary reaction.

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Kinetics Studies of Radical-Radical Reactions
The $NO_2 + N_2H_3$ System

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Fall 2013 Technical Meeting, Western States Section of the Combustion Institute, Colorado State University

October 7-8, 2013

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N_2H_4 + NTO Hypergolic Ignition

- N_2H_3 and NO_2: major components of N_2H_4 + NTO earlier ignition
- NTO consists of structural conformers:
  NO_2, sym-N_2O_4 (D_{2h}), *cis*-$ONONO_2$, *trans*-$ONONO_2$
- Hypergolicity of hydrazine/N_2O_4 :

N_2H_4 + *cis*-$ONONO_2$ $\rightarrow$ $HONO_2$ + $H_2NN(H)NO$ (k_{1a})
N_2H_4 + *trans*-$ONONO_2$ $\rightarrow$ $HONO_2$ + $H_2NN(H)NO$ (k_{1b})
$H_2NN(H)NO \rightarrow N_2H_3 + NO$ (k_2)

$k_1 = 4 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} ($\geq$ 250 K)
$k_2 = 1 \times 10^7$ s^{-1} (1000 K)
(M.C. Lin *et al*., *Chem. Phys. Lett,* **2012**, *537*, 33)

- Fast exothermic reactions:
  N_2H_3 + NO_2 (Radical + Radical) $\rightarrow$ addition $\rightarrow$ products
  N_2H_3 + N_2O_4 (Radical + Stable) $\rightarrow$ abstraction $\rightarrow$ products

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Motivation: $NO_2 + N_2H_3$

- *Practically*
  - ❑ Occurs with negative energy barrier and large exothermicity, significant importance in N_2H_4 + NTO ignition
- *Theoretically*
  - ❑ Occurs via a complex reaction mechanism
  - ❑ Multireference characters of wavefunction are significant due to the electron repulsion between electronegative O and N atoms
  - ❑ Quantitatively correct description of the electron correlation in presence of configurational quasi-degeneracy effects
  - ❑ Chemically accurate representation of exact molecular wave function, and exact energy for prediction of accurate rate coefficient

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Theoretical Approach

- Electronic Structure Calculations
  - Geometries optimization and ro-vibrational frequencies by multireference second-order perturbation theory (CASPT2) with aug-cc-pVDZ or aug-cc-pVTZ basis sets
  - For R + R addition and abstraction, the energies were extrapolated the CBS limit from those of CASPT2/aug-cc-pVQZ and CASPT2/aug-cc-pVTZ
  - For dissociation of addition adducts, the energies were extrapolated the CBS limit from those of CCSD(T)/cc-pVQZ and CCSD(T)/cc-pVTZ
- Kinetic Rate Coefficients
  - Two transition state theory for submerged energy barriers
  - Microcanonical TST at E/J resolved level
    - rigid-rotor harmonic-oscillator assumptions
    - tunneling correction with asymmetric Eckart potentials
    - Master equation analysis via an eigenvector based approach
    - Exponential down energy transfer models
    - Lennard-Jones collision rates

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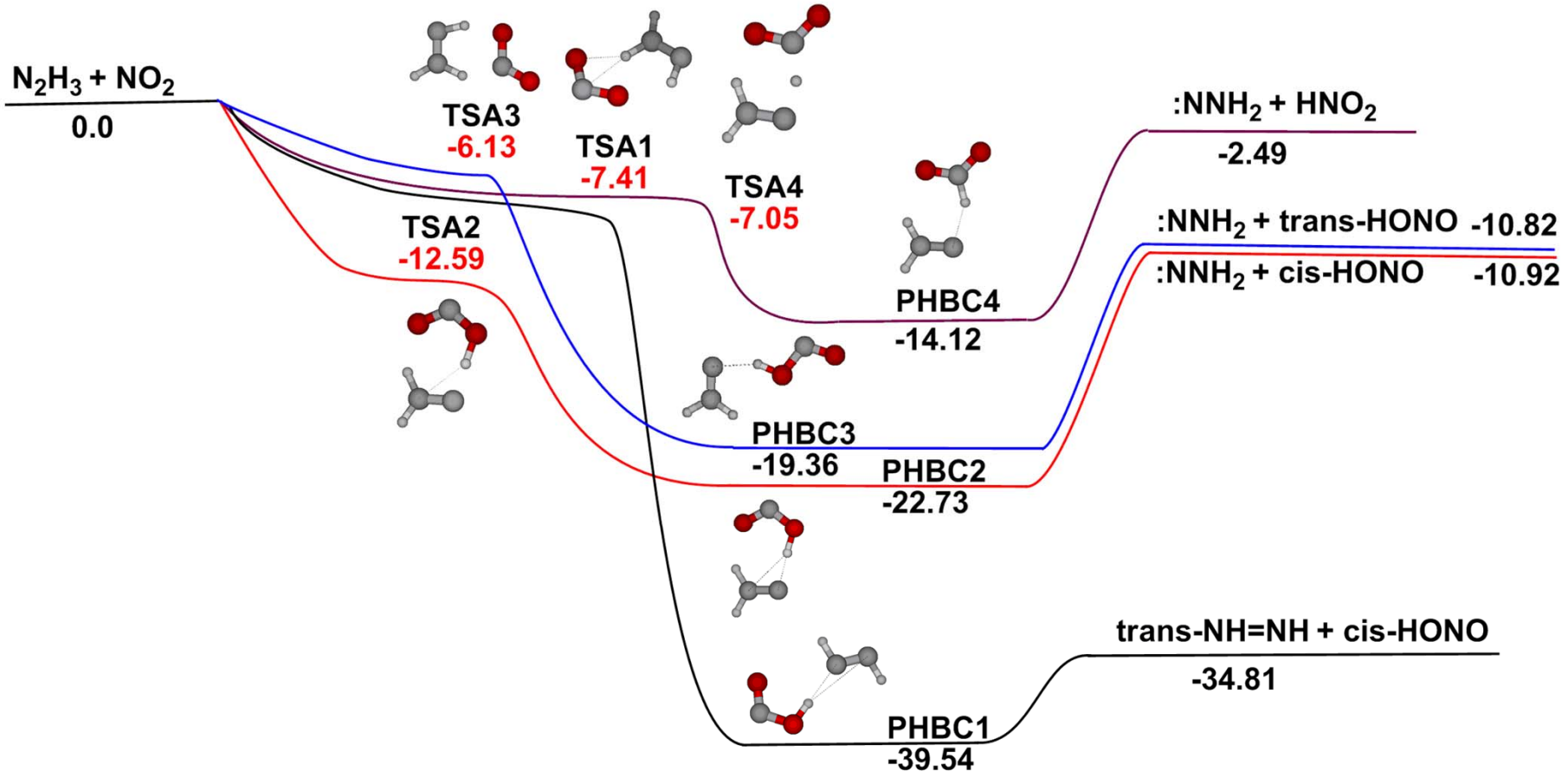
$N_2H_3 + NO_2$ (Abstraction)

Unit: kcal/mol



CASPT2/CBS

RCCSD(T)/CBS//CASPT2

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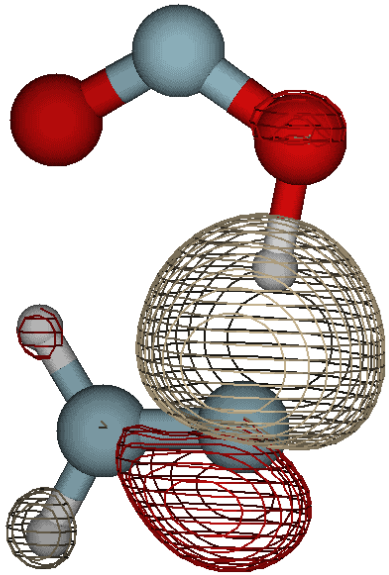
TSA2 → NNH_2-cisHONO



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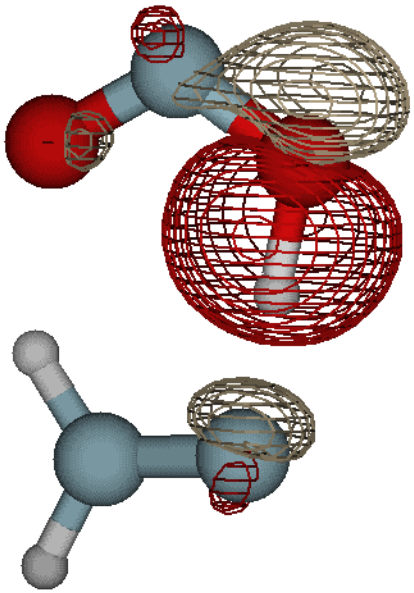

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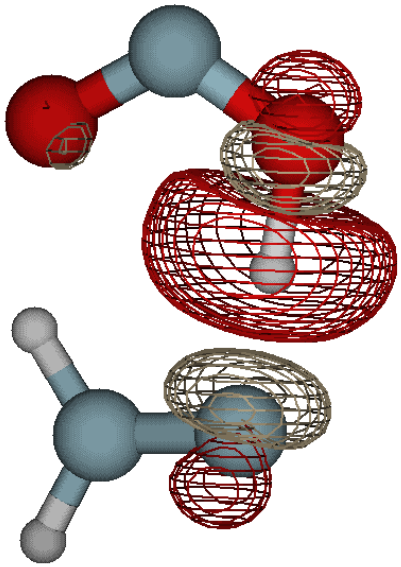

21.1

Optimized at the CASPT2(4e,3o)/aug-cc-pVTZ level

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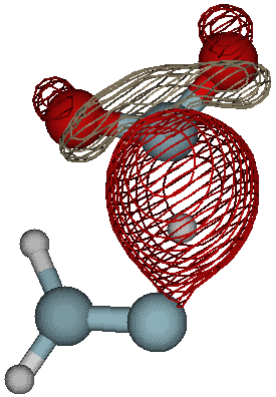
TSA4 → NNH_2-HNO_2



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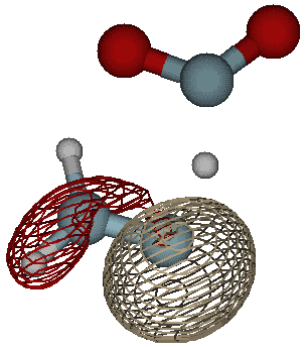

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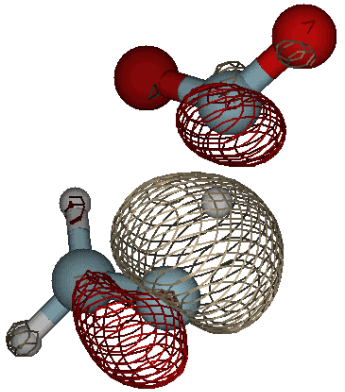

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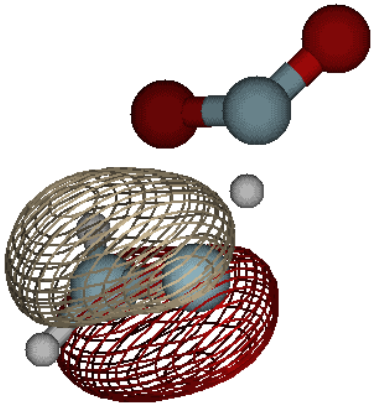

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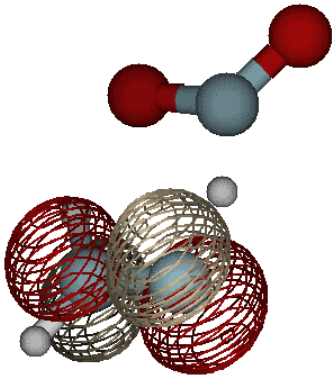

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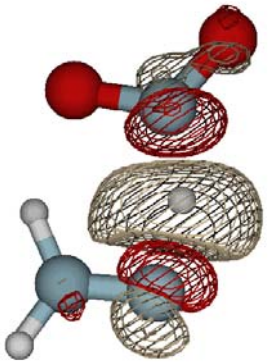

22.1

Optimized at the CASPT2(8e,6o)/aug-cc-pVDZ level

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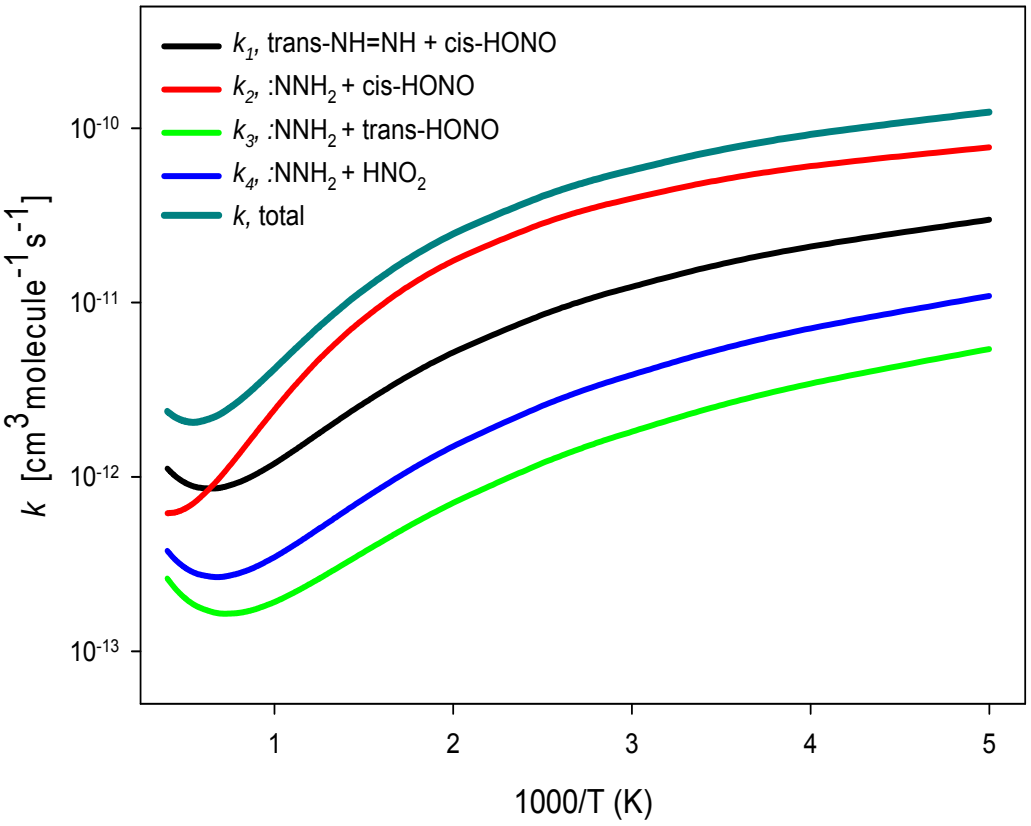
Rate Coefficients: Abstraction

$N_2H_3 + NO_2$



- Inner TS
  - Covalent bond formation
  - Energy barriers:CASPT2/CBS
  - Rigid rotor harmonic oscillator
- Outer TS
  - Phase space theory
  - Long range isotropic potential (Georgievskii & Klippenstein, J. Chem. Phys. 2005)
- Effective TS

$$\frac{1}{N^{\dagger}_{eff}} = \frac{1}{N^{\dagger}_{inner}} + \frac{1}{N^{\dagger}_{outer}}$$

$$k^{\infty}(T) = \frac{1}{hQ_R} \int N^{\dagger}_{eff}(E,J) e^{-E/k_b T} dE dJ$$

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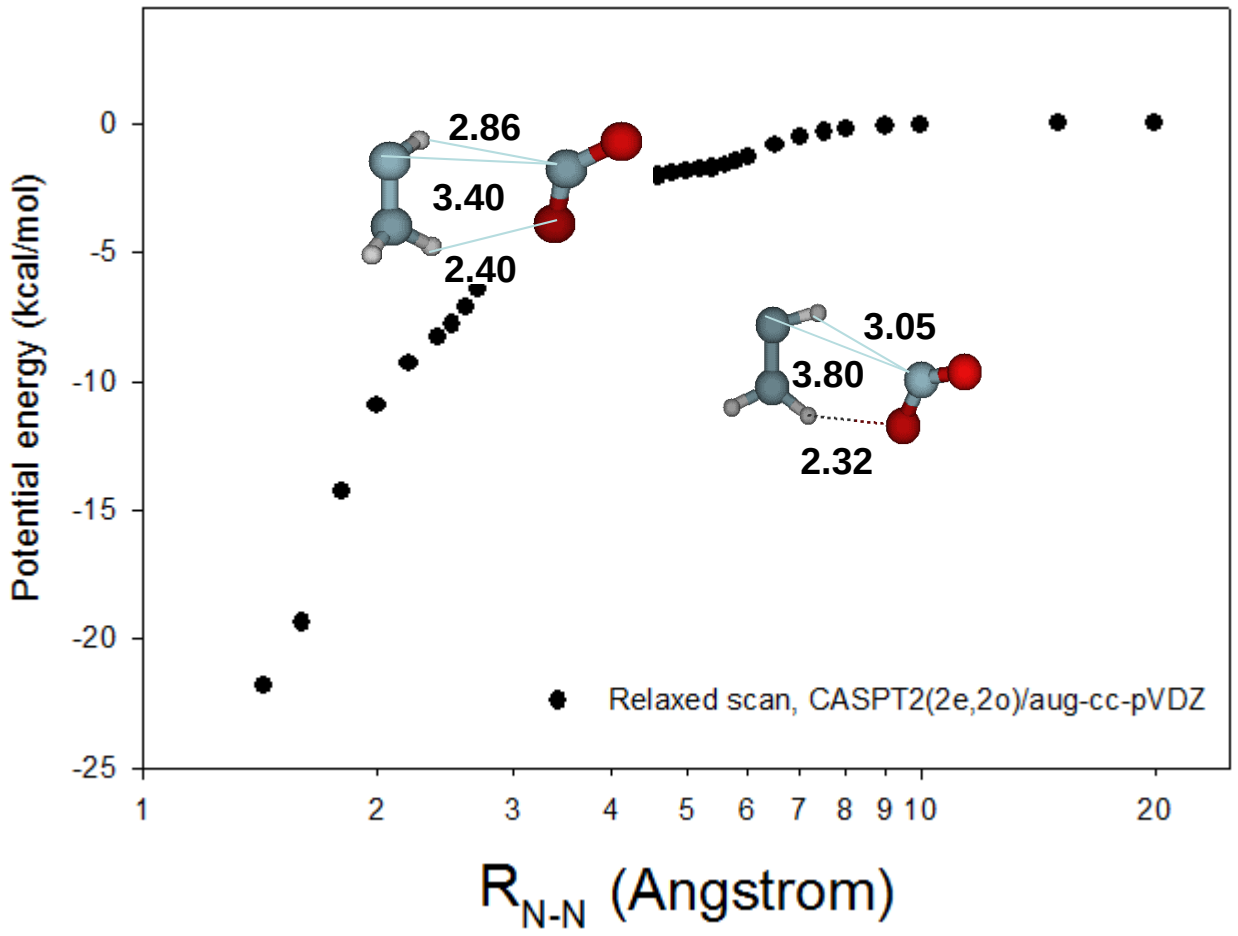
N–N Addition Potential

$\Delta H^o_{f,\ NHNH_2}$ = 55.3 kcal/mol

$\Delta H^o_{f,\ NO_2}$ = 7.9 kcal/mol



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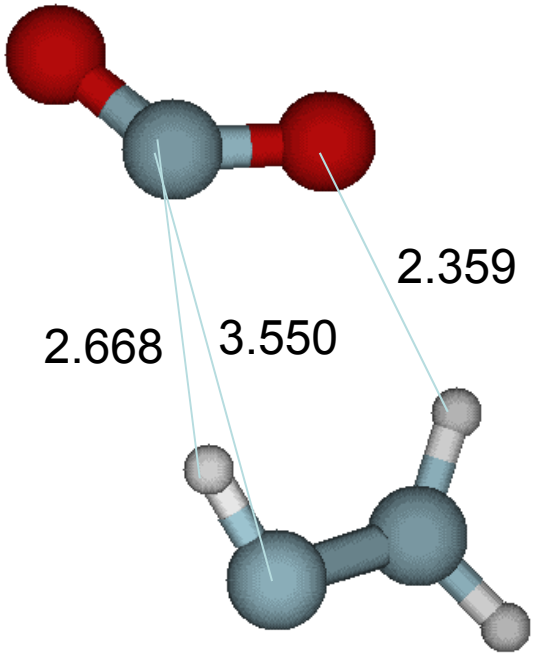
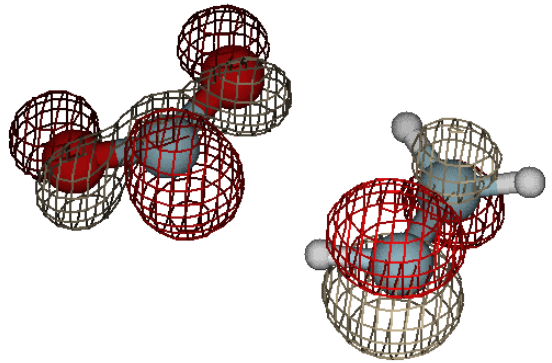
Addition of $N_2H_3 + NO_2$



TS1 (*i*32.35 cm^{-1})



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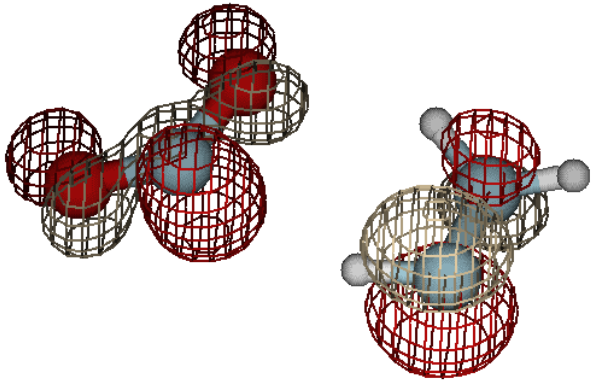

21.1

Ground state destabilization:
orbital splitting (p_π - p_π repulsion) on NO_2

Optimized at the CASPT2(2e,2o)/aug-cc-pVDZ level

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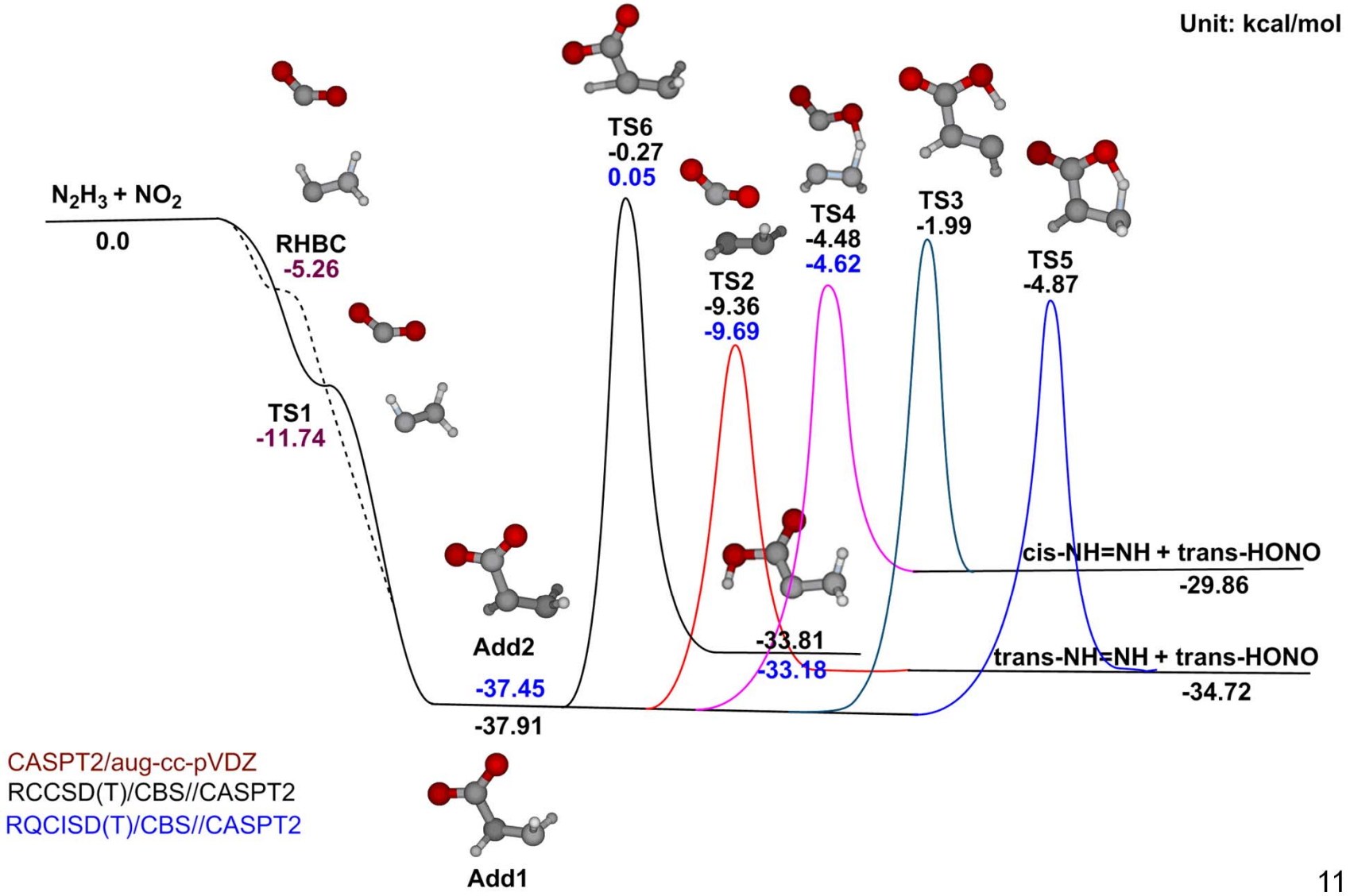
PES of N_2H_3 + NO_2 (Addition)



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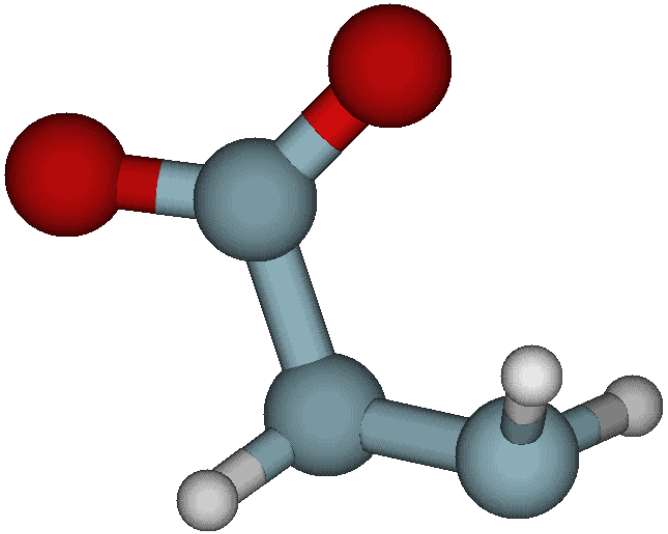
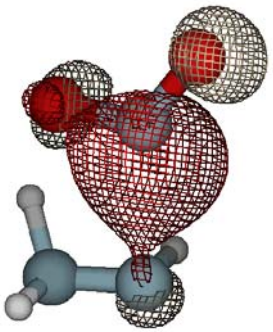
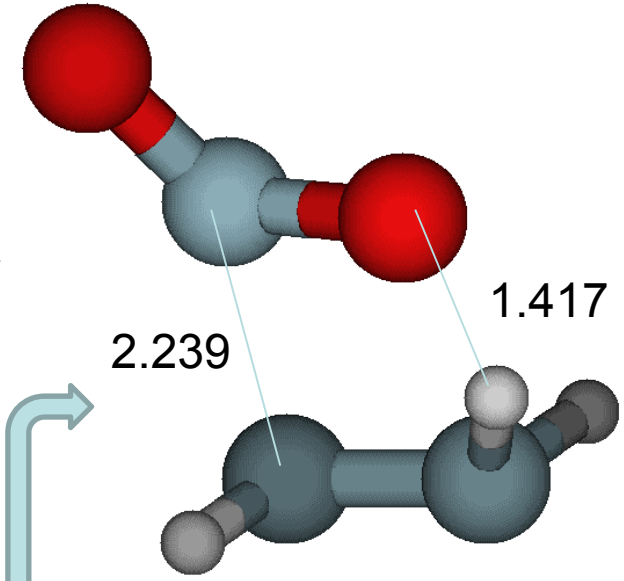
N_2H_3-NO_2 Adduct Decomposition



Adduct-1





TS3

*i*1067.05 cm-1

CASPT2(8e,6o)/aug-cc-pVDZ

Electron transfer for N-N bond breaking
Thermodynamic product stability

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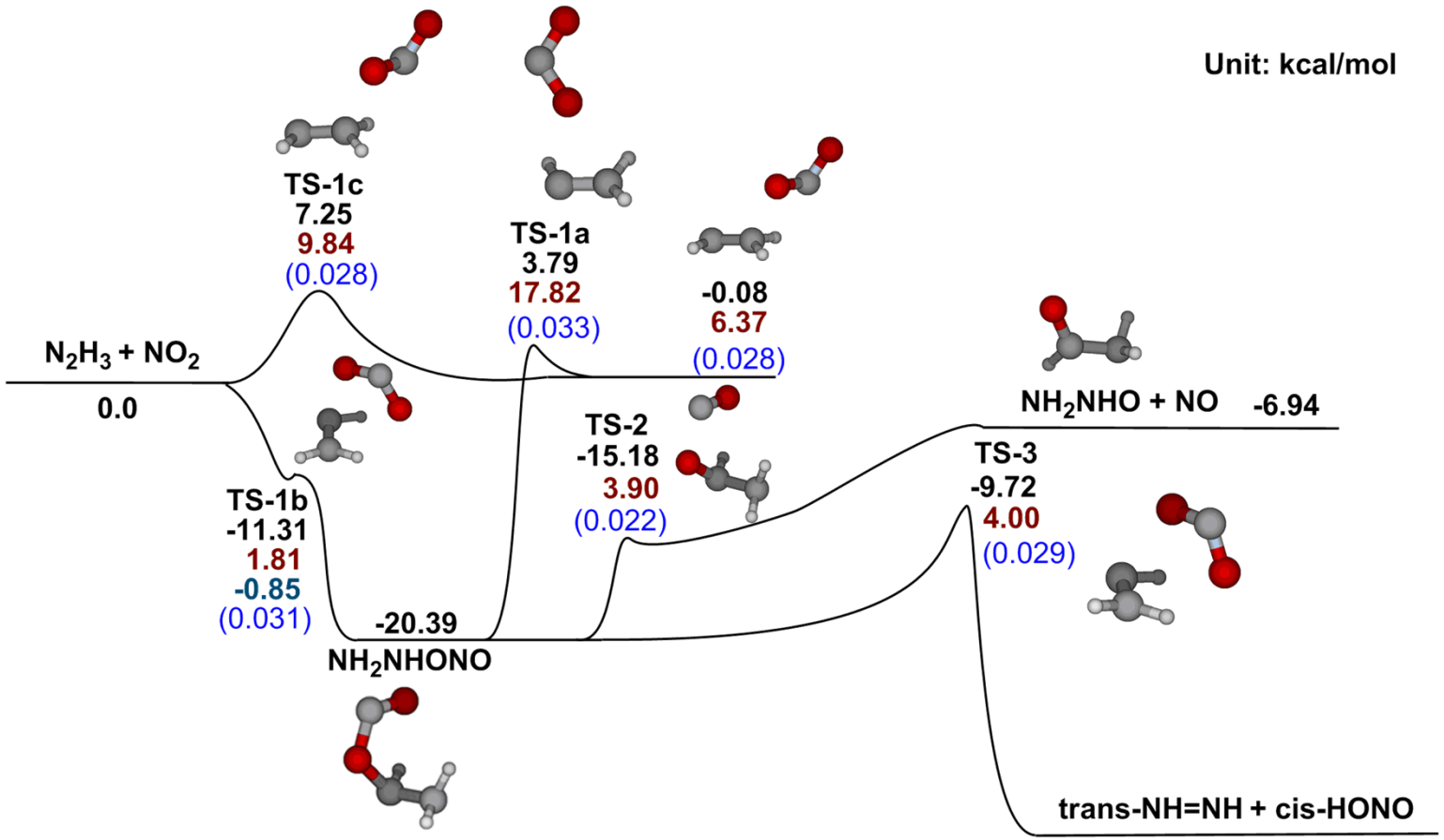
PES of N_2H_3 + NO_2 (Addition)



CASPT2/aug-cc-pVDZ
CASPT2/aug-cc-pVTZ
RCCSD(T)/CBS//CASPT2
T1 diagnostic: RCCSD(T)/cc-pVQZ//CASPT2

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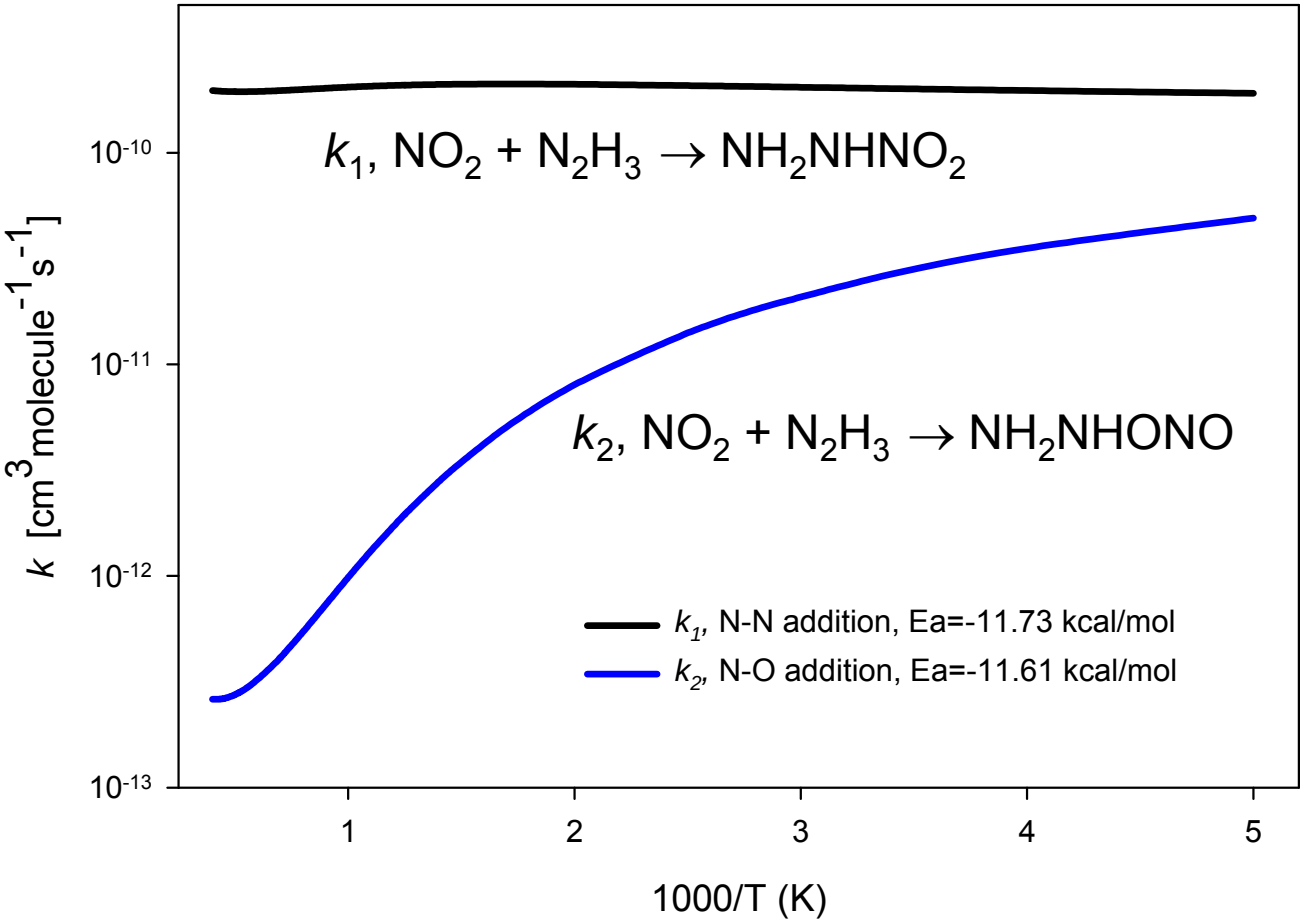
Rate Coefficients: Addition



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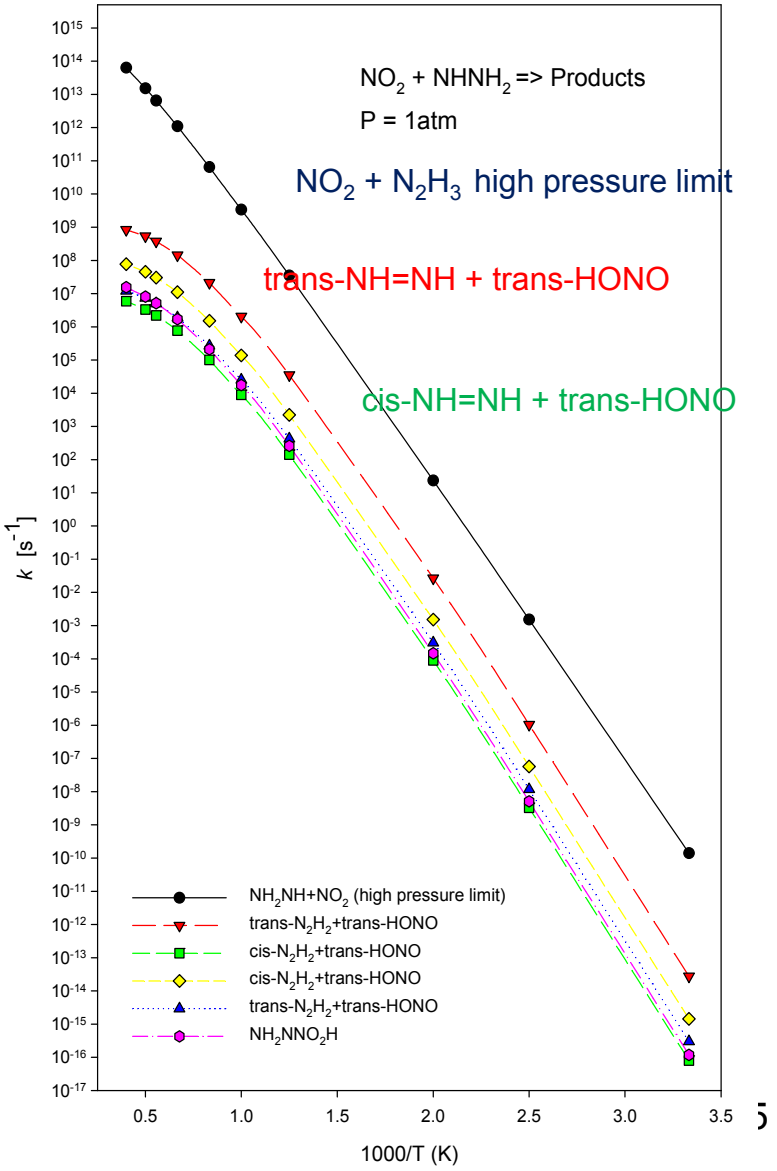
Rate Coefficients: Dissociation

- Microcanonical TST at the E/J resolved level employing rigid-rotor harmonic-oscillator assumptions
- The pressure-dependent kinetics analysis using single-well master equation for irreversible dissociation at the E/J resolved level
- The collisional energy transfer probability was approximated by:
  $\Delta E_{down} = 200 \times (T/300)^{0.85}\ cm^{-1}$
- The Lennard-Jones parameters for collision rates were estimated to be $\sigma = 4.84$ Å and $\varepsilon = 441\ cm^{-1}$



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Concluding Remarks

- Four abstraction channels were found with the negative energy barriers up to 12 kcal/mol, and product H-bonded complexes have 5 - 12 kcal/mol energies stable than the dissociation products
- Abstraction by the nucleophilic O atom forming trans-N_2H_2 + cis-HONO is exothermic to 34.8 kcal/mol, forming NNH_2 + cis-HONO is the dominant channel
- The NO_2 addition to the N_2H_3 radical proceeds via a complex mechanism. The N–N addition is more favorable than the N–O addition
- The predominant channel for the dissociation of the N–N addition adduct is an intramolecular H-transfer to form the trans-HONO + trans-N_2H_2 products

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Acknowledgements

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